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QUANTITATIVE X-RAY DIFFRACTION ANALYSIS OF CHROMIUM(III) DOPED TRICALCIUM SILICATE PASTES

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ABSTRACT

The hydration products of tricalcium silicate (C_3S)* pastes prepared with different concentrations of Cr^{III} solutions have been investigated (w/s ~ 0.5). Tricalcium silicate is the main constituent of Portland cement responsible for the strength and stability of hardened Portland cement paste. $Cr(NO_3)_3.9H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$, added as dopants to C_3S, simulate trivalent chromium waste that may be stabilized in ordinary Portland cement. X-ray diffraction was used to monitor the development of the hydration reaction products from the early stages to the late reaction stages. Leaching studies were carried out to evaluate the stability of the Cr^{III} containing phases in the hydrated C_3S matrix.

When added in the trivalent form, chromium has been found to be primarily contained in C_3S pastes as calcium chromium hydroxide complexes. The nature of the complex formed depended on the ambient conditions within the reaction chamber. The concentration of the chromium complexes were also found to vary considerably with both age and the chromium concentration in the initial Cr^{III}/C_3S mixture. Cr^{III} was found to be totally stabilized in C_3S paste and immobile in the standard acetic acid leaching test.

Introduction

Ordinary Portland cement (OPC) is conventionally used to immobilize Cr^{III} liquid wastes prior to disposal in landfills. The complexity of OPC hydration coupled with the chemistry of Cr^{III} solutions have been an impediment to comprehensively understanding the reasons behind the stabilization of Cr^{III} in solidified cement matrices. A simplified Cr^{III}/C_3S system is commonly employed since C_3S is the most important component of OPC, and its hydration product, C-S-H (calcium silicate hydrate) is responsible for the strength and stability of OPC pastes [1 - 3]. Recently, Kindness et al. [2], found that Cr^{III} is immobilized in C_3S due to the

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*Cement notations: C = CaO; S = SiO_2; A = Al_2O_3; F = Fe_2O_3; H = H_2O; CH = $Ca(OH)_2$; C_3S = Ca_3SiO_5; C-S-H = Calcium Silicate Hydrate.

formation of an insoluble chromium hydroxide. This theory differs from earlier controversial conclusions that Cr^{III} replaces Si or Ca in C-S-H [3 - 7]. In other experiments by Kindness et al. [2], involving Cr^{III} and some Portland cement components, C_3S, CH, C_3A and C-S-H were doped with 0.0019 M and 0.0048 M Cr^{3-} at a w/s ratio of ~ 100. The CH/Cr^{III} system hydrated at 55°C indicated the formation of a compound similar to $Ca_2Al(OH)_7.3H_2O$. The compound was fitted to a hexagonal cell and the formula $Ca_2Cr(OH)_7.3H_2O$ was proposed. At 25°C, an isomorph of $Ca_2Al_2O_5.3H_2O$ was observed (Ca/Cr = 0.28). All XRD reflections were broad and diffuse. Similar products were observed in the C_3A/Cr^{III} systems. Based on these observations, it was concluded that chromium could substitute for aluminum in most of the calcium aluminate hydrate phases present in OPC. In addition to $Cr(OH)_3.3H_2O$ observed in C_3S/Cr^{III} pastes, a crystalline phase containing primarily Ca and Cr in a Ca/Cr ratio of ~ 0.74 was observed. About 2 wt% Si was admixed with the Ca - Cr phase. Leaching experiments conducted by Bishop et al. [8] suggest that the initial concentration of Cr^{III} in the leachate decreases with increasing surface area of cement/heavy metal admixture. They attributed this to the higher leachate pH around smaller Portland cement particles. This occurs because small particles were found to leach alkalinity more rapidly than large ones. Leaching studies by Roy et al. [6] also indicate that Cr^{III} concentration in the leachate does not become noticeable until a breakdown in C-S-H occurs through Si dissolution. This supports the likelihood that Cr is incorporated in C-S-H.

This investigation attempts to identify and quantify the crystalline Cr^{III} containing phases in solidified wastes by x-ray diffraction. Leaching studies are also carried out to evaluate the stability of Cr^{III} in C_3S paste.

Materials and Methods

The preparation of the C_3S used in this study has been discussed elsewhere [9]. Table 1 shows the concentrations of the Cr^{III} solutions employed in the immobilization experiments and the hydration times of the simulated waste forms. Reagent grade $Cr(NO_3)_3.9H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ were obtained from Aldrich Chemicals (Wisconsin, USA).

TABLE 1
Hydration Experiments Detailing Concentrations of Chromium Solutions and Hydration Times

Solution *(Solution/C_3S ~ 0.5 by wt)*		*Molarity (M)*	*Hydration Period (min-minutes; hrs-hours; d-days; mths-months)*					
			5 min	*6 hrs*	*24 hrs*	*72 hrs*	*60 d*	*14 mths*
Cr^{III}	Chromium nitrate	0.1			*		*	
		1			*		*	
		2	*	*	*	*	*	
		2.75						*
	Chromium chloride	0.1			*		*	
		1			*		*	
Standard	Distilled water				*		*	*

* - *Hydration periods of sample.*

Ten grams of C_3S were separately mixed with 5 ml of each chromium solution to make a paste. To serve as a standard, 5 ml of distilled water were also mixed with 10 g of C_3S. The pastes were cast into plastic molds and stored (uncovered) in a humidifying chamber plugged with ascarite and flushed with N_2. Curing under N_2 is essential because carbonation occurs much faster in the relatively small laboratory samples than in the very large quantities of waste/cement containment systems encountered in practice. Two sets of 2.75 M Cr^{III} paste were prepared. One set was exposed to the humidity in the chamber like the other samples, while the second set was sealed in a polyethylene bottles and placed in the humidifying chamber.

Except for the 60 day and 14 month old samples, all other samples were injected with isopropyl alcohol to stop the hydration reaction. This was followed by evacuation in a vacuum desiccator for 18 hours. The 60 day old samples were simply evacuated for 24 hours. All samples were stored in a vacuum desiccator prior to analysis.

X-Ray Diffraction. X-ray diffraction patterns were recorded on a Rigaku X-ray Diffractometer equipped with a rotating anode, utilizing CuK_α radiation at 40 kV and 110 mA. Several primary standards were employed. C_3S was taken from the stock kept under vacuum. $CaCO_3$ was from the same batch as the starting material for C_3S preparation. $Ca(OH)_2$ was obtained by calcining $CaCO_3$ at 1000°C until a constant weight was achieved. The resulting CaO was transferred to a stoppered flask and hydrated in excess distilled water for 24 hours. The slurry was filtered in a CO_2 free environment (glove bag) and dried at 105°C for 1 hour.

Five grams of each primary standard were mixed with 1 g of rutile (internal standard). The mixture was ground to particles < 5mm in size using cyclohexane as grinding aid. Five grams of each hydrated sample were ground in a similar manner with 1 g of rutile. No rutile was added to samples meant for routine qualitative analysis.

The data collection strategy was similar to that used by Gutteridge [10]. A sample was loaded from the back into a 20 mm x 3 mm cylindrical hole drilled into a glass slide [11]. For all samples, diffraction intensities were obtained between 5 and 55°2θ at 40 kV and 110 mA. The diffractometer was step scanned at 0.05° intervals for 10 seconds per interval. For the primary standards, the background was fitted with a cubic spline and subtracted. In the hydrated samples, the amorphous C-S-H diffuse halo was simulated and subtracted from the pattern.

By using a cubic spline interpolation routine, the rutile (110) peak was aligned to 27.4501 ± 0.0005°2θ. This required interpolating the original 1000 data points to 5000 data points. Each pattern was collected in triplicate. The rutile (110) peak was then normalized to 1000 counts. A linear least squares procedure was used to calculate the weight fractions of the primary standards in the sample. The reliability (R) is given as:

$$R = \frac{\sum_{i=1}^{5000}\left[(y_i)_s - \left(\sum_{j=1}^{M} w_j (y_i)_j + c_i\right)\right]^2}{\sum_{i=1}^{5000}\left[(y_i)_s - c_i\right]^2} \qquad (1)$$

$(y_i)_s$ is the ith data point of sample s, $(y_i)_j$ is the ith data point of the primary standard j, w_j is the weight fraction of the primary standard j in the sample, M is the number of primary standards and c is the contribution of the background to the ith data point. c also accounts for the amorphous halo. The w_j coefficients in the equation were obtained using a Gaussian elimination routine. The amorphous C-S-H was obtained by difference (1 - sum of w_i).

Leaching. Leaching tests were carried out on the 14 month old hydrated pastes using the EPA Standard Toxicity Characteristic Leaching Procedure (TCLP) [12]. A sample was ground to a powder with a particle size < 0.5 mm and leached with acetic acid (pH 2.88). 200 ml of acetic acid were added to the 10 g sample in a high density polyethylene bottle. The bottle and its contents were agitated in a rotary shaker at 30 rpm for 18 hours. A Perkin-Elmer 4000 atomic absorption spectrometer (AAS) was used to analyze the leachate solution. The leachate was acidified with 1 M HNO_3 to bring the pH to below 3. This prevented precipitation of the metal ions prior to analysis.

Results and Discussions

Fig. 1 shows the x-ray powder patterns of 2 M Cr^{III} pastes hydrated for varying times. The strong peaks at 27.4, 36.1, 41.2 and 54.3°2θ are due to rutile (TiO_2), added to all the pastes

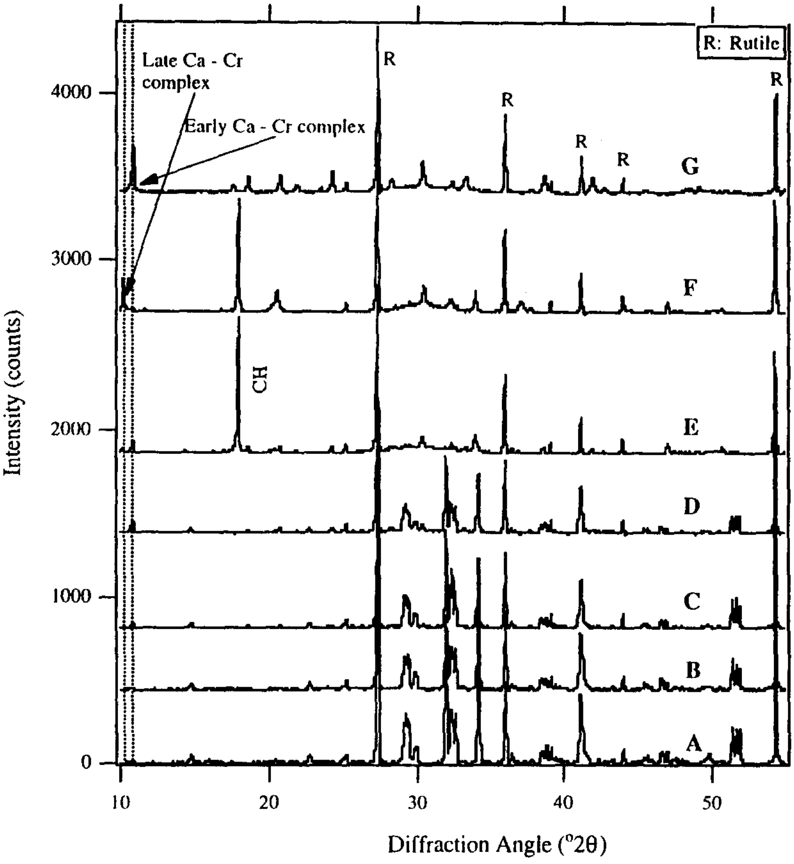

FIG. 1.

XRD patterns of 2 M Cr^{III} pastes hydrated for; (A) 5 minutes, (b) 6 hours, (C) 24 hours, (D) 72 hours, (E) 60 days, (F) 2.75 M Cr^{III} - 14 months exposed and (G) 2.75 M Cr^{III} - 14 months - sealed.

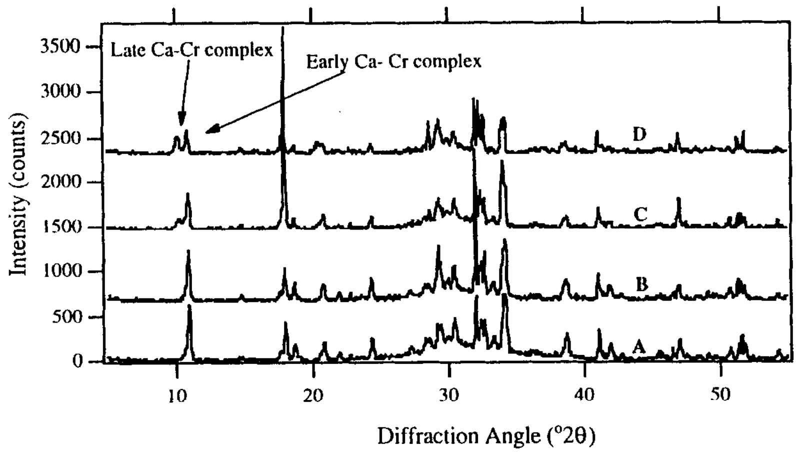

FIG. 2.

XRD patterns of 15 day old 2 M Cr^{III} pastes: (A) compacted-sealed, (B) uncompacted-sealed, (C) compacted-exposed and (D) uncompacted-exposed.

as a standard. The presence of equal amounts of a standard enabled peak alignment and quantification of the crystalline phases.

Within the first five minutes of reaction, no extra peaks apart from the starting C_3S peaks were observed even though some C_3S had reacted (Fig. 1a). Conduction calorimetric studies [13] indicate a high heat of solution within a few seconds of the reaction. After 24 hours, a phase with its strongest peak at 11°2θ began to emerge (Fig. 1c). This phase is not one of the normal hydration products of C_3S. The diffraction intensities of this phase increased continuously with time up to 72 hrs (at least). In the 60 day old paste however (Fig. 1e), another set of peaks with the most intense peak at 10.1°2θ could be discerned. X-ray microanalyses revealed that these phases contained calcium and chromium with no silicon [13]. For brevity throughout the text, the phase that was first noticed in the 6 hr old 2 M Cr^{III} paste is referred to as 'early Ca-Cr complex' and the phase that was first observed in the 60 day old 2M Cr^{III} paste as 'late Ca-Cr complex'. In the completely hydrated 2.75 M Cr^{III} paste (14 month old), exposed to a humidifying chamber (Fig. 1f), the early Ca - Cr complex had dissolved completely leaving only diffraction intensities of the late Ca - Cr complex. CH was also present. For the sealed 2.75 M Cr^{III} paste (Fig. 1g), also hydrated for 14 months, no decomposition of the early Ca - Cr complex occurred. To establish the cause of decomposition of the early Ca - Cr complex, 2 M Cr^{III} pastes were prepared and hydrated for 15 days under different conditions.

TABLE 2

QXRD of 2 M Cr^{III} Pastes Hydrated for Varying Times

Hydration Time	*C_3S (wt%)*	*$Ca(OH)_2$ (wt%)*	*Early Ca-Cr complex*	*Late Ca-Cr complex*	*Reliability (Equation 1)*
5 min	62.0	n.d*	n.d	n.d	0.02
6 hrs	51.1	n.d	7.22	n.d	0.03
24 hrs	48.1	n.d	8.6	n.d	0.02
72 hrs	37.2	n.d	12.9	n.d	0.03
14 mths (sealed)	n.d	2.4	28.6	n.d	0.03

* n.d - not detected.

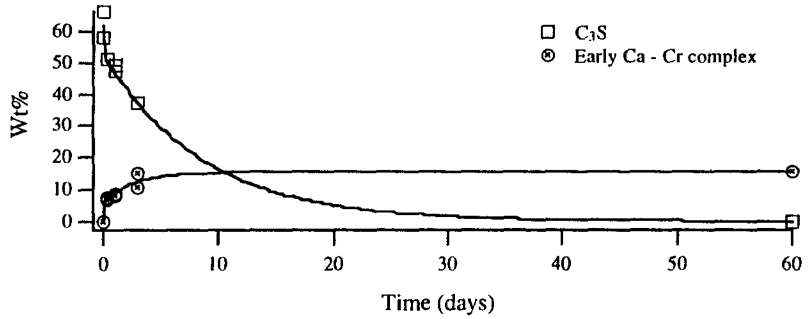

FIG. 3.
Rate of reaction of C_3S and formation of early Ca - Cr complex.

Fig. 2 highlights these experiments. Two sets of 2 M Cr^{III} doped pastes were cast in plastic molds without covers and placed in a N_2 flushed humidifying chamber. One of the two sets was compacted to obtain a monolithic block of waste after setting and the other was cast straight into the mold without compaction. Two other sets were sealed in plastic bottles with only one compacted. A striking observation is the presence of the early Ca-Cr complex in the sealed pastes (Figs 2a and 2b) and the presence of both early and late Ca-Cr complexes in the pastes exposed to the humid atmosphere (Figs 2c and 2d). It is also apparent that the pressure exerted during compaction did not appreciably affect the course of reaction in the sealed pastes, but reduced the decomposition of the early Ca - Cr complex in the exposed pastes. Water was found to collect on top of the exposed pastes with large single crystals of CH adhering to the surfaces. The presence of single crystal CH accounts for the extensive preferred orientation exhibited by the (001) CH peak at 18.1°2θ. Some CH had also formed in the sealed pastes but was different in morphology than the visible crystals obtained in the exposed pastes. These are indications that CH formed in the sealed and exposed pastes are of different origins. Since the emergence of single crystal CH coincides with the development of late Ca - Cr complex and an attendant reduction in the early Ca - Cr complex, the following reaction sequence appears most plausible:

$$\text{Early Ca - Cr complex} \xrightarrow[\textit{decomposition}]{H_2O} \text{Late Ca - Cr complex} + \text{CH} + H_2O \tag{2}$$

TABLE 3
QXRD Analyses of Partially Hydrated 0.1 M and 1 M Chromium Pastes

Sample	*C_3S (wt%)*	*$Ca(OH)_2$ (wt%)*	*$CaCO_3$ (wt%)*	*Reliability (Equation 1)*
Blank - 24 hrs	72.2	9.5	n.d	0.016
0.1M CC - 24 hrs	65.4	11.2	n.d	0.018
0.1M CN - 24 hrs	68.3	8.6	0.3	0.009
1M CC - 24 hrs	61.6	2.7	n.d	0.019
1M CN - 24 hrs	67.9	n.d	n.d	0.007
Blank - 60 d	44.5	17.7	0.8	0.007
0.1M CC - 60 d	36.3	18.7	2.3	0.018
0.1M CN - 60 d	33.0	20.75	0.8	0.007
1M CC - 60 d	2.9	12.6	0.3	0.005
1M CN - 60 d	1.2	13.2	n.d	0.006
Blank - 14 mths	7.6	31.9	1.7	0.014

CC = $[Cr(H_2O)_4Cl_2]Cl.2H_2O$; CN = $Cr(NO_3)_3.9H_2O$

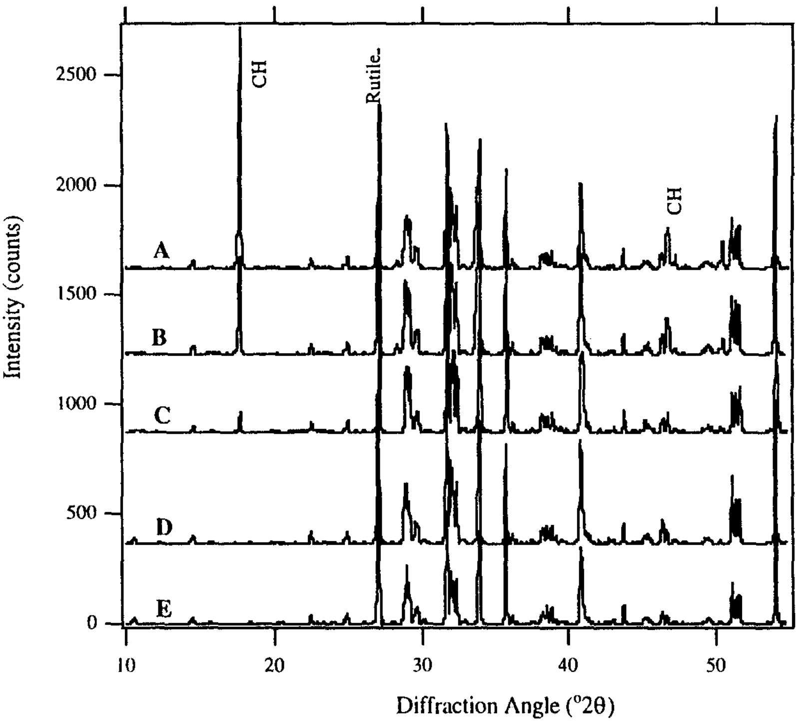

FIG. 4.

XRD patterns of 24 hour old CrIII pastes; (A) 0.1 M Cr chloride (B) 0.1 M Cr nitrate, (C) 1 M Cr nitrate, (D) 1 M Cr chloride and (E) 2 M Cr nitrate.

The excess water absorbed from the humidifying chamber activates the decomposition reaction. The stoichiometry of the equation was ignored because the exact chemical formulae of the Ca - Cr phases are unknown. Formation of single crystal CH and collection of water on the surfaces of solidified pastes were also noticed in the 1 M, 2 M and 2.75 M Cr^{III} doped pastes hydrated for longer than 72 hours.

Judging from the amorphous C-S-H halo in Fig. 2, the formation of C-S-H does not appear to be overly affected by the hydration conditions. An interesting observation was the coloration of the different Ca - Cr complexes. The paste hydrated for 5 minutes was deep green while the pastes containing the early Ca - Cr complex had a distinct purple tinge. A gray coloration was observed in pastes containing the late Ca - Cr complex.

The diffraction pattern of the late Ca-Cr complex did not match any previously characterized compound in the powder file. The diffraction pattern of the early Ca - Cr complex closely matched the pattern of $Ca_6Al_2O_6(NO_3)_6 \times H_2O$ (JCPDS 28-0208). However, no symmetry or lattice parameter determination was carried out for this phase. Only peak positions were identified. The chromium analogue was produced by reacting 2 M chromium nitrate with CH as shown in Equation 3.

$$6Ca(OH)_2 + 2Cr(H_2O)_6^{3+} + 6(NO_3)_3^- + xH_2O \rightarrow [Ca_3Cr(OH)_6.(NO_3)_3]_2.12{+}xH_2O \quad (3)$$

The diffraction pattern indicated a single phase and was used as the primary standard for the early Ca - Cr complex. The late Ca - Cr complex could not be synthesized. Several unsuccessful attempts were made to produce single crystals to facilitate structure determination

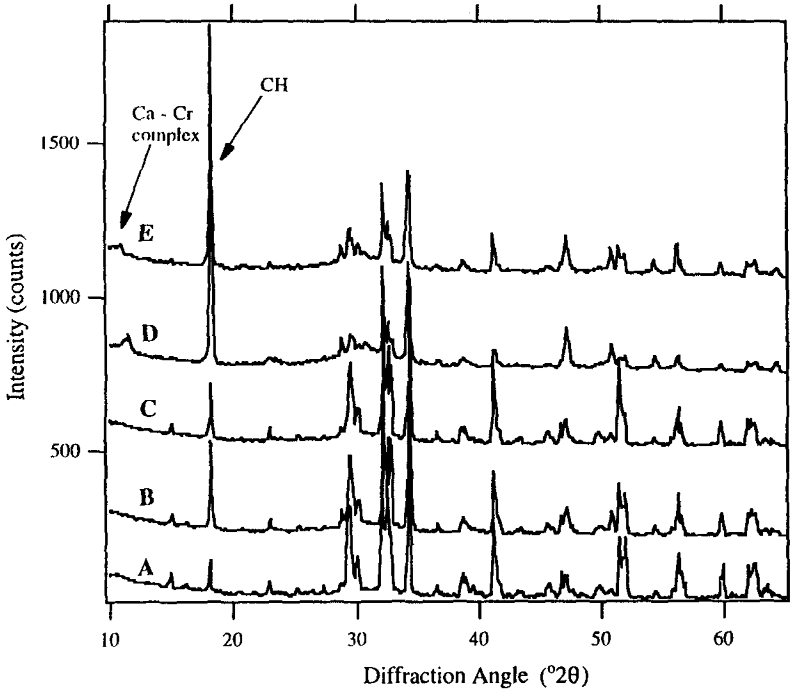

FIG. 5.
XRD patterns of 60 day old blank and Cr^{III} pastes; (A) Blank, (B) 0.1 M Cr chloride, (C) 0.1 M Cr nitrate, (D) 1 M Cr chloride and (E) 1 M Cr nitrate.

with x-ray diffraction. The compositions of some of the 2 M pastes hydrated for varying times are shown in Table 2. The pastes containing the late Ca-Cr complex were not analyzed because no standard could be synthesized. The rate of C_3S dissolution, and the rate of formation of early Ca - Cr complex, are shown in Fig. 3.

Enumerated in Table 3 are the compositions of 0.1 M and 1 M Cr^{III} doped pastes. These pastes were hydrated for 1 and 60 days to identify specific effects of increasing Cr^{III} concentrations on the reaction mechanism. Both chromium nitrate and chromium chloride were used to better understand the role of the anion. Fig. 4 shows the diffraction patterns of 24 hour old 0.1 M and 1 M Cr^{III} pastes. In the 0.1 M chromium nitrate and chromium chloride pastes, none of the Ca-Cr complexes were observed within the detection limit of the x-ray diffractometer.

The overall diffraction patterns are similar to the 1 day old blank paste with only CH and unreacted C_3S prominent. A small amorphous C-S-H halo had also started forming. In the 1

TABLE 4
AAS Leachate Analyses of Standard and Cr - Doped Pastes Subjected to TCLP Leaching

Sample	*Ca(ppm)*	*Cr(ppm)*	*Si (ppm)*	*pH*
2.75M CN-14 mths (exposed)	5950	0.2	< 2	12.1
2.75M CN -14 mths (sealed)	5560	0.3	< 2	11.7
Early Ca - Cr complex	7390	0.2	< 2	8.8
Blank - 14 mths	3480	< 0.2	< 2	12.5

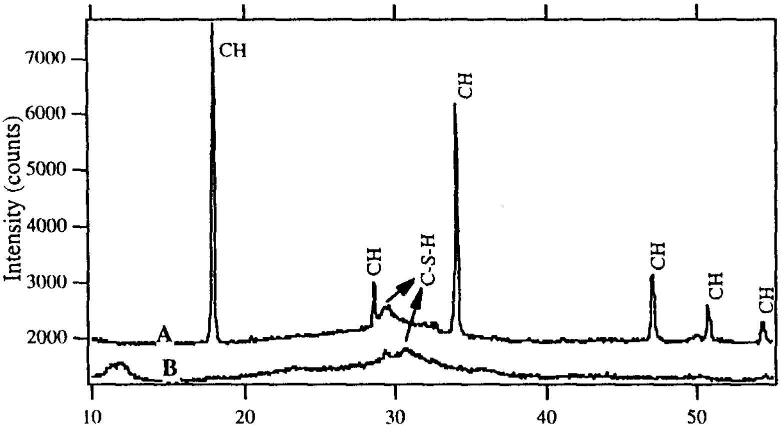

FIG. 6.

XRD patterns of leached pastes; (A) 14 month old blank and (B) 14 month old 2.75 M Cr^{III}.

M chromium nitrate, however, a weak peak at ~ 11°2θ indicates the presence of early Ca-Cr complex. This peak is located at 11.2°2θ in the 1 M chromium chloride paste. The slight shift is not unexpected as Cl^- modifies the structure of the Ca-Cr complex. After 24 hours, very little CH has formed in the 1 M Cr^{III} pastes and none in the 2 M Cr^{III} paste. As shown in Table 2, no CH was observed even after 72 hours in the 2 M Cr^{III} paste. It is obvious that the early Ca-Cr complex formed preferentially to CH, which did not start forming until all the available chromium had been consumed; hence, increasing chromium concentrations inhibited CH formation.

The diffraction patterns of the 60 day old pastes are shown in Fig. 5 and the composition of the phases in Table 3. The diffraction patterns of the 0.1 M Cr^{III} pastes are similar to the 60 day old blank paste with the amorphous C-S-H halo, CH and unreacted C_3S peaks dominating the powder patterns. In the 1 M chromium pastes, most of the C_3S had reacted leaving strong CH and very weak Ca-Cr complex peaks. The most obvious late Ca-Cr complex peak is located at 30.6°2θ, superimposed on the amorphous C-S-H halo. The peak at 11.2°2θ in the 1 M chromium chloride paste remained. It is obvious from Table 3 that even at low concentrations, chromium accelerates the hydration reaction of C_3S. Chloride ion is a better anion accelerator than nitrate ion, during the early stages of reaction.

The relatively low reliability values in some of the patterns is mainly due to the C-S-H standard used to simulate the amorphous halo, and the possible presence of amorphous chromium compounds especially during the early hydration periods.

Leaching Studies. The leaching studies were aimed at confirming the similar leaching characteristics that exist between the much investigated ordinary Portland cement and tricalcium silicate.

Results of AAS analysis of leachates are shown in Table 4. These represent the approximate leachate concentrations after 18 hours of the acetic acid leaching procedure (TCLP). No Si was detected in the leachate in any of the samples (detection limit ~ 2 ppm). Similar to the established notion, Cr^{III} was found to be immobile under the acetic acid leaching procedure. In the blank pastes, the high pH and Ca contents of the leachates are primarily due to the dissolution of CH and some CaO units in the C-S-H.

The leached blank paste still has some CH with a strong (001) preferred orientation (Fig. 6). In the leached 2.75 M Cr^{III} exposed paste, in addition to dissolution of CH, most of the diffraction intensities attributed to the late Ca - Cr complex have disappeared. Coupled with the high Ca content of the leachate (higher than the Ca content in the blank leachate which has more CH), Ca ions in the complex were leached out leaving behind an amorphous chromium complex. Since an alkaline leachate solution (pH ~ 11.9) is in contact with the solid throughout the leaching experiment, insoluble chromium oxide or hydroxide complexes should be responsible for the continued immobilization. Identical results were obtained for the sealed 2.75 M Cr^{III} paste.

Conclusions

- Two types of Ca - Cr complexes were identified in Cr^{III} doped C_3S pastes. The early complex generally starts to form within a few hours, increasing in concentration until most of the Cr has been consumed. If the reacting paste is exposed continuously to water vapor in a humidifying chamber, this early complex decomposes within a few days to form CH and a late Ca - Cr complex. In an environment devoid of additional moisture, the early Ca - Cr complex is retained at the completion of hydration.
- Chromium hydroxide was not observed in the hydrated C_3S/Cr^{III} systems studied. This is contrary to the observation of Kindness et al. [2].
- Cr^{III} accelerates the reaction of C_3S. The accelerating effect increases with increasing Cr^{III} concentrations.
- Both $Cr(NO_3)_3.9H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ form Ca - Cr complexes. However, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ is a better accelerator than $Cr(NO_3)_3.9H_2O$, especially during the early stages of hydration. This is primarily due to the anion effect. Cl^- is known to be a better accelerator than NO_3^- [14].
- Continued immobilization of Cr^{III} in the pastes subjected to acetic acid leaching procedure, may be attributed to the formation of insoluble chromium oxide or hydroxide complexes.

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